

SEQUENTIAL INDUCTION OF CHIRALITY IN POLY(PHENYLACETYLENE)S

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Several hierarchical levels of chirality have been detected in functionalized poly(phenylacetylene)s (PPA).¹ In this work we have studied the chirality induction throughout these levels in PPA functionalized with phenylglycine methyl ester groups, Fig. 1.² These pendant groups force the PPA chain to lose its planar *all-transoid* shape to form helical structures. The chiral seed of the pendants, [(*R*)- or (*S*)-], dictates the preferent handedness of the helices, both the internal polyacetylene helical covalent backbone and the external helix formed by the side pendants which forms a complementary helix or counter-helix. In this work, we afford a full assessment of the interconnection between stereocenter and helix sources of chirality and the action of these polymers as chiral templates of other supra-molecular structures with inherited chiral properties. We then used VCD spectroscopy to demonstrate the chiral induction from the stereogenic centers to the backbone helix and from this to the pendant helix, which are largely promoted by two mechanisms: steric effects and hydrogen bonding. In addition, the VCD spectra supported that the helical setup of the pendants induces the solvent DMSO molecules to adopt a solvation helix around the polymer, thus proving how an achiral solvent becomes chirally organized owing to the template effect of the covalent polymer helices. A similar effect was observed in DMSO solutions of the monomeric units. Interestingly, this resulted in opposite helical sense to the one observed in the polymer with identical enantiomeric form.

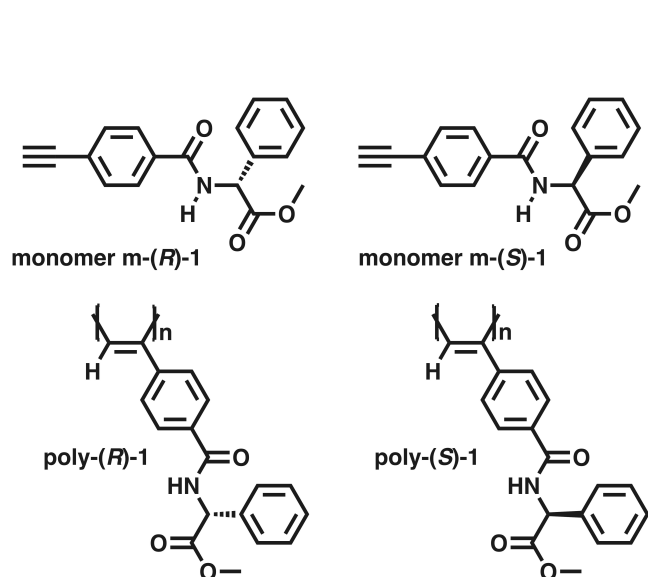


Figure 1. Chemical structures of poly-(*R*)-1 and poly-(*S*)-1 and their constituent monomers.

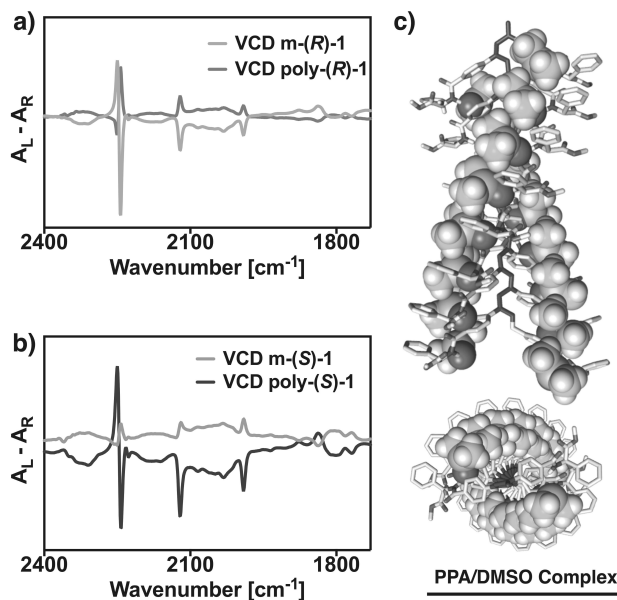


Figure 2. a) VCD spectra of *m*-(*R*)-1 and poly-(*R*)-1 (b) VCD spectra of *m*-(*S*)-1 and poly-(*S*)-1 recorded as solutions in DMSO-*d*₆. b) 3D model (c) of the helical arrangement of the DMSO molecules around a phenylglycine-PPA polymer.

References

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